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# A PRELIMINARY INVESTIGATION OF GOETHITE PRECIPITATION

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# A PRELIMINARY INVESTIGATION OF GOETHITE PRECIPITATION

by

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## ABSTRACT

A preliminary investigation of goethite ($\alpha$FeO.OH) precipitation was carried out with the threefold purpose of determining the importance of oxygen supply during precipitation, of assessing the adsorptive-desorptive properties of goethite and of characterizing some commercial goethite residues with special reference to their silver contents. Under conventional commercial synthesis conditions in sulphate media, the formation of goethite is critically dependent on the rate of oxygen supply and to a lesser extent on the mixing of the oxygen with the liquid phase. Although the synthetic products consisted only of goethite, the iron contents were less than the theoretical amount for FeO.OH, and all precipitates contained $\sim$3% $SO_4$. Commercial goethite residues adsorb significant amounts of both cations (e.g., $\sim$10% Zn) and anions (e.g., $\sim$10% $SO_4$). These ions can be partly eliminated by extensive washing with hot water or 4 M $NaNO_3$; acid washing dissolves the goethite and actually increases the degree of adsorption. Silver is not eliminated by any of the washing procedures. The adsorptive

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properties of goethites will greatly complicate any fundamental synthesis investigations of this compound. Four commercial goethite residues were characterized mineralogically and chemically. All were similar and consisted of poorly crystallized αFeO.OH with minor amounts of sphalerite, zinc ferrite, zinc oxide, silicate gangue and gypsum. Silver phases were not detected in any of the residues although all contained this element in moderate amounts (60-90 ppm Ag).

# EXAMEN PRÉLIMINAIRE DE LA PRÉCIPITATION DU GOETHITE

par

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## RÉSUMÉ

On a effectué un examen préliminaire de la précipitation du goethite ($\alpha$FeO.OH), dont le triple but était de déterminer l'importance de l'apport en oxygène lors de la précipitation, d'évaluer les propriétés d'adsorption et de désorption du goethite et de caractériser certains residus commerciaux du goethite, particulièrement en ce qui a trait à leur contenu en argent. Dans des conditions de synthèse commerciale classiques en milieu sulfate, la formation de goethite dépend très étroitement du taux d'apport d'oxygène et à un moindre degré, du mélange de l'oxygène avec la phase liquide. Bien que les produits synthétiques étaient constitués seulement de goethite, les contenus en fer étaient inférieurs à la quantité théorique de FeO.OH et les précipités contenaient environ 3% de $SO_4$. Les résidus commerciaux de goethite adsorbent une quantité importante de cations (~10% Zn, par exemple) et d'anions (~10% de $SO_4$). On peut éliminer en partie ces ions en lavant les résidus à l'eau chaude ou à l'acide (4 M $NaNO_3$). Ce dernier procédé dissout le goethite et augmente en fait le degré d'adsorption. Aucun des procédés de lavage n'élimine l'argent. Les propriétés d'adsorption du goethite vont compliqué grandement toutes les études fondamentales sur la synthèse de ce composé. On a effectué la caractérisation minéralogique et chimique de quartre résidus commerciaux de goethite. Tous les échantillons analyés étaient semblables et étaient constitués de $\alpha$FeO.OH faiblement cristallisé et de petites quantités de sphalerite, de ferrite de zinc, d'oxyde de zinc, de silicate de gangue et de gypse. On n'a détecté de phases d'argent dans aucun des résidus bien que contenaient cet élément en quantité modérée (60 à 90 ppm Ag).

# INTRODUCTION

During the hydrometallurgical processing of base metal ores or concentrates, large amounts of iron inevitably pass into solution. At some point in the processing circuit, the iron must be rejected in a form which can be readily filtered and washed free of associated solution. This problem is especially acute in the zinc industry where, for many concentrates, iron-rich solutions are a direct consequence of high zinc recoveries. It has been shown that iron can be precipitated conveniently as jarosite, goethite or hematite, and these compounds form the basis of three industrial processes. The jarosite process is the oldest, and both the practice and theory of this technology have been discussed (1,2,3). Although the jarosite process is effective and offers many processing advantages, it suffers from the need to purchase an "alkali" and from the large volume of residue produced for each tonne of iron precipitated (i.e., jarosites contain $\sim$30% Fe and have a density of about 3.2 g/cm$^3$). The hematite process (4) offers a more stable precipitate of low volume (i.e., hematite contains $\sim$70% Fe and has a density of about 5.3 g/cm$^3$), but requires a pressure vessel for its formation. In some respects, the goethite process is a technological compromise between the jarosite and hematite technologies. It offers a more compact residue (i.e., goethite contains $\sim$62% Fe and has a density of $\sim$4.3 g/cm$^3$) than jarosite, but does not require a pressure vessel as is the case for hematite.

Two commercial goethite processes have been developed. In the Vieille Montagne technique (5,6), the solution from the hot acid leaching of zinc calcines that contains a significant $Fe^{3+}$ concentration is reduced with concentrate to form $Fe^{2+}$. After liquid-solid separation, the reduced solution is oxidized with air while maintaining the pH in the 2.5-3.5

range with calcine additions. Goethite is readily formed and can be easily filtered and washed to form a residue suitable for impoundment. In the Electrolytic Zinc process (7,8), the ferric-bearing solution from the hot acid leach is added to a large volume of solution containing <1 g/L $Fe^{3+}$ at 80-90°C such that the removal rate of $Fe^{3+}$ as goethite is equal to the rate of $Fe^{3+}$ addition. Again, the pH is regulated at >2.5 to ensure the formation of goethite. In both processes, efforts are made to ensure that the concentration of $Fe^{3+}$ at the time of precipitation is <1 g/L. Such low $Fe^{3+}$ concentrations (the concentration of $Fe^{2+}$ is immaterial) are necessary for the production of FeO.OH not contaminated with other iron compounds (9).

Goethite ($\alpha$FeO.OH) is but one of three polymorphic forms of FeO.OH. To some extent, the goethite process is a misnomer since commercial precipitates can contain other constituents such as $\beta$FeO.OH and $\alpha Fe_2O_3$ (8). Although conventional knowledge assumes that $\alpha$FeO.OH is formed from sulphate media, and $\beta$FeO.OH from chloride solutions, the actual situation has been shown to be very much more complex (2) with concentration, anion type, temperature and impurities all playing a major role in determining which phases are precipitated. Because of the poor crystallinity of the phases, X-ray diffraction methods alone are sometimes not a reliable technique for characterizing the products and recourse must be made to DTA-TGA, IR-spectroscopy, microprobe analysis, etc. for a definitive identification; this greatly adds to the difficulty of obtaining reliable information on the nature of the products. Not only are the conditions giving rise to $\alpha$, $\beta$ or $\gamma$FeO.OH unclear, but the issue is further clouded by the co-precipitation of $\alpha Fe_2O_3$ (hematite) as shown by Davey and Scott (8). Hematite appears to be the thermodynamically most stable form of iron

at all temperatures (10); i.e., the following reaction is thermodynamically favourable.

$$2\alpha FeO.OH \longrightarrow \alpha Fe_2O_3 + H_2O \qquad (1)$$

Thus, the formation of goethite is due to subtle thermodynamic differences like the surface energies of the fine-grained precipitates (11) and to nucleation effects. Temperatures in the range 25-100°C also affect the relative proportions of goethite and hematite (12). The issue is further complicated by the precipitation of $Fe(OH)_3$ or basic iron sulphates which can subsequently transform into FeO.OH or hematite (13) depending on the temperature of the solution and its composition. At 100°C only $Fe_2O_3$ was found by Collepardi et al. (14), whereas mixtures were observed at 60-80°C. Chloride ion accelerates the formation of $Fe_2O_3$. The question of ferric precipitates and their aging is also of some practical concern since some workers have postulated that goethite nucleates on such material which, of course, would contaminate the product. For example, Ohyabu and Ujihira (15) postulated that goethite grew from (and on) an incipient jarosite core. Margulis et al. (16) suggested that goethite formed from amorphous precipitates of a basic iron sulphate or a hydrated iron oxide. For nucleation on any sulphate-bearing phase (15,16), the goethite would likely be contaminated by the sulphate remaining in the nucleus, and such contamination would have practical implications for concerns the potential use of the goethite residue.

Although the formula for goethite is FeO.OH, most commercial and synthetic precipitates made from $ZnSO_4$-bearing media contain large and variable contents of $SO_4$ and Zn (6,7). Although some of the impurity elements are present as entrained solution, a major fraction seems to be adsorbed and/or incorporated into the goethite structure. Even natural

goethites which have had long times to equilibrate with their surroundings contain significant amounts of adsorbed ions (17). Removal of such adsorbed species is of concern both for the safe environmental storage of goethite residues and for their potential utilization.

The question of silver losses in goethite precipitates remains largely unanswered. Virtually nothing is known about the nature or extent of silver incorporation into synthetic goethite precipitates. Furthermore, the distribution of silver in zinc plants employing goethite precipitation has not been reported.

Some of the factors affecting the precipitation of goethite have been elucidated (5,7). Goethite was readily made above 65°C with the rate increasing slightly with increasing temperature; no apparent activation energy was reported. The extent of Zn and $SO_4$ incorporation in the residue decreased with increasing synthesis temperature, but was always significant. Increasing the solution pH from 2.2 to 3.5 approximately doubled the rate of iron removal. There is no agreement on the effect of seeding. Since the Vieille Montagne method relies on the simultaneous oxidation and precipitation of iron, it is not surprising that the rate of goethite formation, for that technique, is strongly dependent on both the rate of stirring and the volume of air injected into the solution (5). The oxidation of $Fe^{2+}$ in the presence of iron precipitates, such as FeO.OH, has received little attention whereas the corresponding reaction in homogeneous solution has been extensively investigated (18,19).

The current preliminary investigation had three general objectives. The first purpose was to synthesize goethite and to assess the importance of oxygen input on its formation. Such data would be needed both for any subsequent evaluation of the precipitation parameters and for the determination

of silver losses into synthetic goethite residues. The second goal was to evaluate the extent of ion adsorption-desorption on goethite since this factor would greatly influence the interpretation of impurity incorporation results. The last objective of the study was to determine whether silver appeared in commercial goethite precipitates. For this work, goethite residues were obtained from National Zinc, Bartlesville, Oklahoma, and were studied by both chemical and mineralogical methods to try to characterize them and their silver contents. The operations of National Zinc have been published (20).

## EXPERIMENTAL

The Vieille Montagne precipitation method was employed for all synthesis work since it is the only goethite process yet to find commercial application. In this method, the precipitation is carried out according to the following reactions.

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+ \longrightarrow 2Fe^{3+} + H_2O \qquad (2)$$

$$2Fe^{3+} + 2OH^- \longrightarrow 2Fe(OH)^{2+} \qquad (3)$$

$$2Fe(OH)^{2+} + 2H_2O \longrightarrow 2FeO.OH + 4H^+ \qquad (4)$$

$$4H^+ + 4OH^- \longrightarrow 2H_2O \qquad (5)$$

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 4OH^- \longrightarrow 2FeO.OH + H_2O \qquad (6)$$

The synthesis work was done in a 2-L reaction kettle fitted with 4 Ti baffles and a variable speed stirrer with a Ti impeller; one litre of solution was used. The kettle was heated in an oil bath controlled at $75 \pm 0.3^{\circ}C$. The pH during reaction was controlled ($\pm 0.1$ pH units) automatically by pumping 2.0 M LiOH solution to compensate for the OH ions

consumed by Equation 6; no local formation of $Fe(OH)_3$ occurred on addition of the LiOH. Lithium hydroxide was used since Li does not form an end-member jarosite-type compound. The 0.3 M $FeSO_4$ solution was reduced with Fe powder prior to the start of the experiment, and was then filtered for use.

The reaction was initiated by adding the $FeSO_4$ solution to the reaction kettle, heating rapidly to temperature and adjusting the pH to the desired value with $H_2SO_4$/LiOH. Oxygen gas was then injected at a given rate through a fritted gas dispersion tube. The flow rate was measured and controlled by a mass flow meter; the gas was preheated by passage through a copper coil also immersed in the oil bath. The gas-slurry was mixed by a variable-speed mechanical stirrer. At the completion of the tests, the slurry was filtered, washed with 2 L of $H_2O$ and dried at 110°C.

The study of the sorptive properties of goethite was done using a commercial goethite residue supplied by National Zinc Company. The residue (∿25 g) was slurried at 70°C with 1 L of $H_2O$, $H_2SO_4$ (0.1-0.8 M) or 4.0 M $NaNO_3$ for ∿30 min. The slurry was then filtered and a few grams of the solid were removed for analysis. The remaining solids were then re-slurried with 1 L of a fresh and similar solution; this procedure was repeated up to five times. The solids were assayed for $Zn^{2+}$, $SO_4^{2-}$ and Ag to evaluate both anion and cation sorption.

To gain some insight into the nature and form of silver incorporation in commercial goethite residues, four products from National Zinc were examined. In addition to classical chemical analysis of the various fractions, the goethite residues were also examined by a variety of mineralogical techniques. X-ray diffraction analysis was carried out

using a 57.3 mm diameter Debye-Scherrer camera with filtered Co $K_\alpha$ radiation ($\lambda$ = 1.7889Å). The various products were mounted in polished sections and were examined both by optical microscopy and by scanning electron microscopy (SEM) with energy dispersive analyzer (EDX) and backscattered electron imagery. Some of the coarser grains were analyzed with a MAC 400 electron microprobe; the data were corrected using a modified version of the EMPADR VII computer program (21). The goethite residues were also investigated by thermogravimetric analysis using a Cahn RG microbalance. The samples were heated in a flowing argon stream (~50 mL/min) at 5°C/min. Graphs were obtained for the weight loss as a function of temperature in the hope of identifying any significant differences in the four residues.

## RESULTS AND DISCUSSION

### PRECIPITATION OF GOETHITE

Figure 1 shows some typical reaction curves realized when 0.3 M $FeSO_4$ solutions were oxidized at 75°C and pH = 3.5 using various $O_2$ flow rates; a constant 300 rpm stirring speed was employed. The rate of reaction was monitored by following the amount of hydroxide ion pumped to maintain the pH at 3.5; two moles of $OH^-$ are required for each mole of iron precipitated (Equation 6). In the Vieille Montagne approach, iron is simultaneously oxidized and precipitated as goethite; hence, it is not surprising that only negligible reaction occurs for a 0 mL/min flow (the tests are run in air so that there is always some oxygen present). The rate increases rapidly for flows in the 0-50 mL/min range, but further increases in the flow rate have a lesser effect. For low degrees of iron precipitation, the rate curves tend to be linear, whereas they fall off sharply for larger

degrees of reaction, likely because of an appreciable drop in the dissolved iron concentration during the course of reaction.

To try to obtain some quantitative indication of the rates, the reaction curves were fitted to a second order polynomial, and an initial rate (i.e., at $Fe^{2+}$ = 0.3 M) was calculated. Figure 2 illustrates the effect of the oxygen flow rate on the initial rate constant for the goethite formation reaction. As anticipated from Figure 1, the rate increases rapidly with increasing flow rates, but eventually becomes insensitive to this parameter. In the current experimental set up, the rate is nearly independent of $O_2$ flows in excess of 400 mL/min. The precipitation reaction is clearly under oxygen supply control for the low flows, but is likely mostly chemically controlled for $O_2$ flows >400 mL/min.

X-ray diffraction analysis of the various products showed that goethite was formed in all instances, but that it was not well crystallized. No impurity phases were detected. Chemical analysis indicated the products to contain ∿59% Fe as opposed to the 62.8% Fe content of FeO.OH; in addition, all precipitates contain ∿3% $SO_4$ in spite of the thorough washing procedure followed. Figure 3 indicates that there is no systematic or significant variation in the product composition as the flow rate is varied. The method by which the $SO_4$ is incorporated into the goethite is not really known. It could be tenaciously adsorbed on the goethite particles (17), it could be present as an amorphous sulphate nucleus (15,16), or it could even be incorporated in the goethite structure.

The effect of the solution stirring speed on the rate of goethite precipitation was also investigated at a constant $O_2$ flow rate of 50 mL/min, and some typical reaction curves are illustrated in Figure 4. In the absence of any stirring, a fairly low rate is obtained suggesting that

air agitation alone does not provide good bulk mixing in this experimental arrangement. Increasing the agitation rate to 100-200 rpm seems adequate to ensure that the oxygenated solution is thoroughly mixed throughout the reaction vessel. Higher agitation rates are without additional significant benefit in this system. Simple sparging of the gas into the solution without mixing results in ∿50% reaction in 4 h whereas ∿85% reaction occurs in this period if the solution is stirred at 600 rpm.

Initial rate constants were also derived for the experiments done to assess the influence of agitation, and these are plotted as a function of the stirring speed in Figure 5. Although there is a modest rate increase on passing from 0 to 100 rpm, the rate of goethite formation is nearly independent of higher degrees of agitation. The goethite precipitation reaction is likely under oxygen mass transport control for low flows and/or low stirring speeds, and both these parameters would have to be maximized to permit the chemical kinetics to be evaluated. Incidentally, it would appear (5) that commercial goethite processes operate in the oxygen transport control region.

## CHARACTERIZATION OF COMMERCIAL GOETHITE PRECIPITATES

At National Zinc Company, the concentrate contains 56.5% Zn, 5.9% Fe, 1.3% Pb, 0.53% Cd, 0.50% Cu and 260 ppm Ag; the roaster product assays 63.2% Zn, 6.5% Fe, 1.6% Pb, 0.62% Cd, 0.60% Cu and 255 ppm Ag. Clearly some Ag is lost during the roasting step and this behaviour seems common throughout the industry. After hot acid leaching of the calcine (20), a solution is produced that contains 13.7 g/L $Fe^{3+}$, 5.3 g/L $Fe^{2+}$, 51 g/L $H_2SO_4$ and 86 g/L Zn. This solution is reduced with concentrate and partly neutralized with calcine to yield a solution assaying 2.8 g/L $Fe^{3+}$,

14.0 g/L $Fe^{2+}$, 3.8 g/L $H_2SO_4$ and 127 g/L $Zn^{2+}$. This solution constitutes the feed to the goethite circuit; the solution at the completion of goethite precipitation contains 0.0 g/L $Fe^{3+}$, 1.2 g/L $Fe^{2+}$ and 143 g/L $Zn^{2+}$.

Four precipitates from the goethite circuit were provided and these were designated as follows:

| Designation | Description |
|---|---|
| G-1 | Light brown colour, washed (4/5/82) |
| G-2 | Light brown colour, from pile (4/5/82) |
| G-3 | Dark brown colour, washed (4/5/82) |
| G-4 | Dark brown colour, from pile (3/30/82) |

The four samples were subjected to chemical and X-ray diffraction analyses and the results are given in Table 1. Mineralogically all the samples are similar and consist of major αFeO.OH (poorly crystallized goethite) together with minor zinc ferrite and various trace constitutents. The ferrite enters with the calcine used to regulate the pH during hydrolysis. Most of the residual sulphur is present as sulphate and there is a moderately high water soluble zinc content despite the fact that all the residues had been washed.

Microscopic study showed all the residues to be generally similar in that they consisted mostly of goethite particles in the 2-25 μm range but with a few particles as large as ∿300 μm. As Figure 6 shows, the goethite was present both as large platy aggregates (<5% of total) and as somewhat smaller globular masses (>90% of total). Detailed study of the globular forms (Figure 7) indicated some platy characteristics although clearly defined habits are not evident. Although both the "light" and the "dark" precipitates are similar in composition (Table 1), microscopic

Table 1 - Chemical and X-ray Diffraction Analyses of the Four Samples Provided by National Zinc

| Sample Number | Chemical Analysis | | | | | | | | X-Ray Diffraction Analysis |
|---|---|---|---|---|---|---|---|---|---|
| | CANMET (%) | | | | | National Zinc (%) | | | |
| | Fe | Zn | $S/SO_4$ | $S_{Tot}$ | Ag(ppm) | Fe | $Zn_{Tot}$ | $Zn_{Soluble}$ | |
| G-1 | 45.93 | 8.46 | 1.64 | 1.79 | 90 | 49.4 | 8.1 | 0.94 | Poorly crystallized αFeO.OH plus minor zinc ferrite. |
| G-2 | 39.70 | 10.6 | 3.34 | 3.60 | 80 | 39.5 | 9.8 | 3.0 | Poorly crystallized αFeO.OH plus minor zinc ferrite. |
| G-3 | 46.83 | 7.59 | 1.47 | 1.71 | 70 | 47.2 | 6.7 | 4.2 | Poorly crystallized αFeO.OH plus minor zinc ferrite. |
| G-4 | 40.68 | 10.4 | 4.09 | 4.4 | 60 | 39.4 | 10.0 | 1.0 | Poorly crystallized αFeO.OH plus minor zinc ferrite. |

examination showed the dark-coloured material to be more uniform in size and lacking some of the finer grained material evident in the light-coloured products as typified by Figure 8. Similar minor variations in precipitate morphology have been evoked previously (22) to account for variations in the colour of FeO.OH precipitates.

Detailed study of the samples on the SEM-EDX indicated FeO.OH as the major phase but also confirmed the presence of numerous trace constituents. Despite the presence of 60-90 ppm Ag in the precipitates, no silver-bearing phases were detected during the detailed examination.

- Sample G-1 contained zinc ferrite, silicates as well as traces of chalcopyrite. Some sphalerite was present as coarse grains that likely were present in the neutralizing calcine.
- Sample G-2 contained traces of sphalerite, silicate and gypsum, present as fine needle-like crystals. Zinc ferrite was present in minor amounts and it had nearly the ideal composition of $ZnO.Fe_2O_3$.

| Element | G-2 | $ZnO.Fe_2O_3$ |
|---|---|---|
| Zn | 27.1 | 27.12 |
| Fe | 46.4 | 46.33 |
| Total | 73.5 | 73.45 |

- Sample G-3 also consisted of major FeO.OH together with minor zinc ferrite and ZnO. The ZnO contained 97.8% ZnO and 3.1% FeO, and analyses of ZnO particles in the various samples yielded FeO contents of 2-9%. Clearly the ZnO is iron-bearing! Sphalerite, silicates and chalcopyrite were also detected in trace amounts in Sample G-3.

- Sample G-4 also contained minor or trace amounts of zinc ferrite, zinc oxide, silicates and sphalerite. A few grains of sphalerite were analyzed on the electron microprobe and yielded the following average composition, in weight percent: Zn 67.0, Fe 2.0, S 31.7, total 100.7.

The most interesting observation from the detailed study of the commercial products is that the goethite particles all contain Zn and S (as $SO_4$). ZnO contents ranged from 8.2 to 10.1% and $SO_4$ values as high as 6.9% were detected. Separate Zn-S phases could not be detected in the FeO.OH particles either by microscopic examination or by microprobe study. The FeO.OH particles (Figure 9) are somewhat porous, however, and fine grained impurities would be difficult to observe. Nevertheless, the microprobe studies coupled with the synthesis work would seem to indicate an intimate association of Zn and $SO_4$ with the goethite, either through incorporation in the structure or via an adsorption mechanism.

The four residues were also examined by thermogravimetric analysis and the thermal decomposition curves realized at a $5^{o}C$/min heating rate are shown in Figure 10. All the goethites behaved similarly during heating although there were some subtle differences among the residues. All the samples begin to loose weight at $\sim 30^{o}C$ and this initial weight loss continues to $\sim 300^{o}C$. This stage of reaction represents the loss of adsorbed $H_2O$ as well as the conversion of goethite to hematite:

$$2FeO.OH \longrightarrow Fe_2O_3 + H_2O \qquad (7)$$

For pure FeO.OH a theoretical weight loss of 10.0% is expected, but higher losses were observed, likely reflecting significant amounts of adsorbed $H_2O$.

| Designation | Weight Loss (30-400°C) |
|---|---|
| G-1 | 11.0% |
| G-2 | 10.5% |
| G-3 | 12.0% |
| G-4 | 11.5% |

The washed residues (G-1, light and G-3, dark) both show a weak inflection at ∿100°C that might be due to a greater degree of $H_2O$ adsorption for these water washed samples.

For pure FeO.OH, no additional weight loss is expected once the goethite had been converted to $Fe_2O_3$ (Equation 7). For the commercial residues, however, a distinct weight loss is observed at ∿650°C that appears to be due to the decomposition of the incorporated $SO_4$ (Table 1).

$$SO_4^{2-} \longrightarrow O^{2-} + SO_2 + \tfrac{1}{2}O_2 \qquad (8)$$

The effect is more significant in the samples taken from the storage piles with their higher $SO_4$ contents.

| Designation | % $SO_4$ | Predicted Loss | Observed Loss |
|---|---|---|---|
| G-1, light washed | 4.91 | 4.1% | ∿4% |
| G-2, light, from pile | 10.00 | 8.3% | ∿8% |
| G-3, dark, washed | 4.40 | 3.7% | ∿4% |
| G-4, dark, from pile | 12.25 | 10.2% | ∿9% |

The TG studies offer no explanation for the different colours of the goethite residues; these colour variations seem to be related more to morphological differences than to chemical composition. The TG investigations do, however, support the conclusion that "real" goethite precipitates, commercial or laboratory, are very much more complex than the simple FeO.OH formula would indicate.

SORPTIVE PROPERTIES OF GOETHITE

The data presented above indicate that adsorbed impurities will greatly complicate any fundamental studies on goethite synthesis and/or impurity incorporation in goethite residues. To try to shed some light on the magnitude of the adsorption problem with respect to total impurity incorporation, various washing tests on the commercial products, available in large amounts, were carried out. Work was done on the two samples (light and dark) from the storage piles since they seemed to contain more adsorbed species (Table 1). Both the light and dark residue were found to behave in a similar manner, and consequently data are presented only for the light material.

Figure 11 illustrates the variations in the Zn, $SO_4$ and Ag contents of the light residue from the storage pile (G-2) as a function of the number of 1-L washes with water at 70°C. There is an initial large drop in both the $SO_4$ and Zn contents that is likely related to the removal of traces of synthetic medium and/or loosely adsorbed ions. The Ag content increases because of the mass reduction caused by the removal of $SO_4$ and Zn; there is no indication that any silver is being dissolved. Following the initial removal of the loosely-bound ions, further washings cause only slight additional reductions in either the Zn or $SO_4$ levels. Part of the zinc in the residue is present as ferrite and would not be removed by water washing. The form of the sulphate in the residue is not really certain, but sulphate seems to be eliminated at a slow but steady rate. This could reflect either a tenaciously adsorbed form of $SO_4$, a poorly soluble basic iron sulphate, sulphate incorporation in the structure of FeO.OH or some combination of all three. The data of Figure 11 indicate that goethite precipitates do not have a clearly defined composition.

All precipitates are likely to include significant amounts of $H_2O$, $SO_4$, Zn, etc. and the resulting composition will reflect, in part, the extent and nature of the washing procedure.

Figure 12 illustrates the composition of the residue (G-2) washed repeatedly in 4 M $NaNO_3$. As before, there is no indication of any silver desorption; the Ag content rises slightly as the mass of the residue is reduced by the elimination of Zn and $SO_4$. The zinc content and especially the $SO_4$ content fall sharply and continuously in the presence of 4 M $NaNO_3$. Four nitrate washings reduce the $SO_4$ content to $\sim$3.6% whereas the same number of water washes result in a $\sim$5.1% $SO_4$ level. The presence of a high ionic strength solution has displaced $SO_4$ from the goethite and this supports the observation that at least some of the associated ionic species are tenaciously adsorbed on the goethite surfaces.

Washing of the residues with sulphuric acid, even dilute 0.1 M $H_2SO_4$, resulted in significant dissolution of the material as can be inferred from Figure 13. The silver content of the residue rises in a nearly linear manner indicating that about half of the residue has dissolved; there is no suggestion of Ag dissolution from the goethite residue. The Zn content falls fairly sharply to about 5% Zn and then increases slightly. The enhanced reduction in the Zn content likely represents dissolution of ZnO and some ferrite by the acid. The increased Zn levels seen at longer washing times reflect the reduction of the mass of the sample; i.e., a more or less constant amount of zinc in a reduced mass of residue. The behaviour of $SO_4$ in the presence of $H_2SO_4$ is instructive. The $SO_4$ level decreases only very slightly for the first two washes (cf. Fig. 11 and Fig. 12) and then increases at about the same rate as Ag, indicating mass effects. Treating the residue with dilute sulphuric acid does not

displace $SO_4$ from the goethite and may actually increase the amount of adsorption. These results reflect not only the ease of goethite dissolution even in dilute acid media but also the fact that the observed product composition will be strongly influenced by the nature of the anions in the washing solution.

Higher acid concentrations did not eliminate $SO_4$ from the goethite residues, but did increase the rate of goethite dissolution. The following dissolved iron concentrations after 1 h of washing at 70°C are instructive.

| $[H_2SO_4]$ | Fe Dissolved (g/L) |
|---|---|
| 0.3 | 6.76 |
| 0.5 | 8.88 |
| 0.8 | 12.0 |

Unlike jarosite-type precipitates, goethite dissolves easily in warm, dilute $H_2SO_4$ and this property would make any acid washing procedure to recover ferrite and unreacted ZnO very difficult.

## CONCLUSIONS

The results of these preliminary experiments indicate that moderately pure goethite ($\alpha$FeO.OH) can be prepared by oxidation of $FeSO_4$ solutions at 75°C and pH 3.5; the precipitates contain $\sim$3% $SO_4$ but yield only a goethite powder diffraction pattern. For low oxygen flows and stirring rates, the reaction is under oxygen transport control; at high oxygen flows with moderate stirring, chemical kinetics seem to dominate.

Commercial goethite residues consist of poorly crystallized $\alpha$FeO.OH together with traces of zinc ferrite, sphalerite, zinc oxide and silicates. All the residues contained significant ($\sim$10%) Zn and $SO_4$ levels that are

closely associated with the FeO.OH. Part of the sulphate can be removed by washing with $H_2O$ or $NaNO_3$, and this suggests that some of this impurity is present in adsorbed form. Goethites are readily soluble in warm $H_2SO_4$ of moderate concentration. The behaviour of impurity ions during precipitation/washing suggests that the product composition will depend on the nature and extent of the washing procedure.

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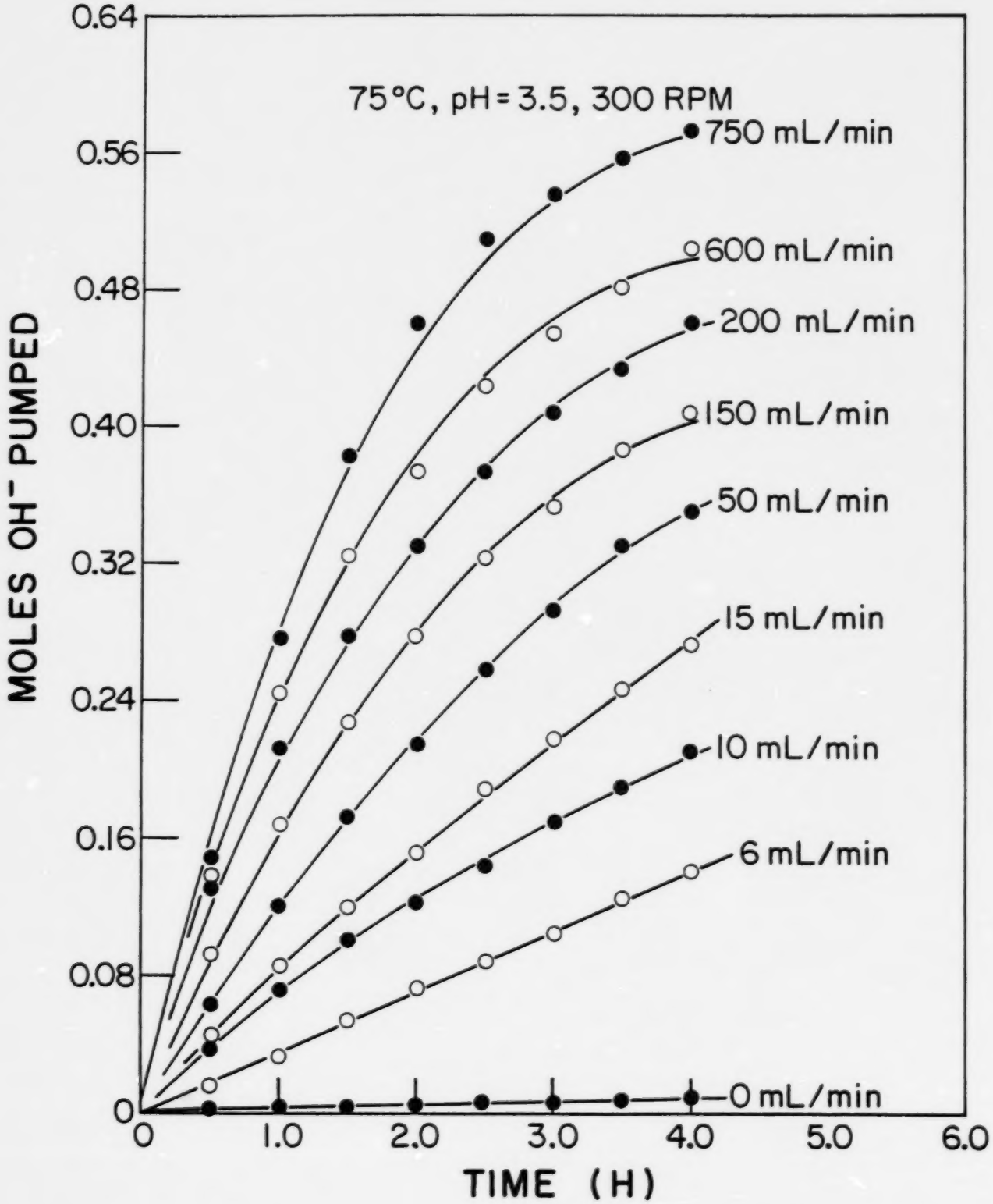


Fig. 1 - Typical reaction curves for goethite precipitation at 75°C, pH 3.5, 300 rpm and various oxygen flow rates.

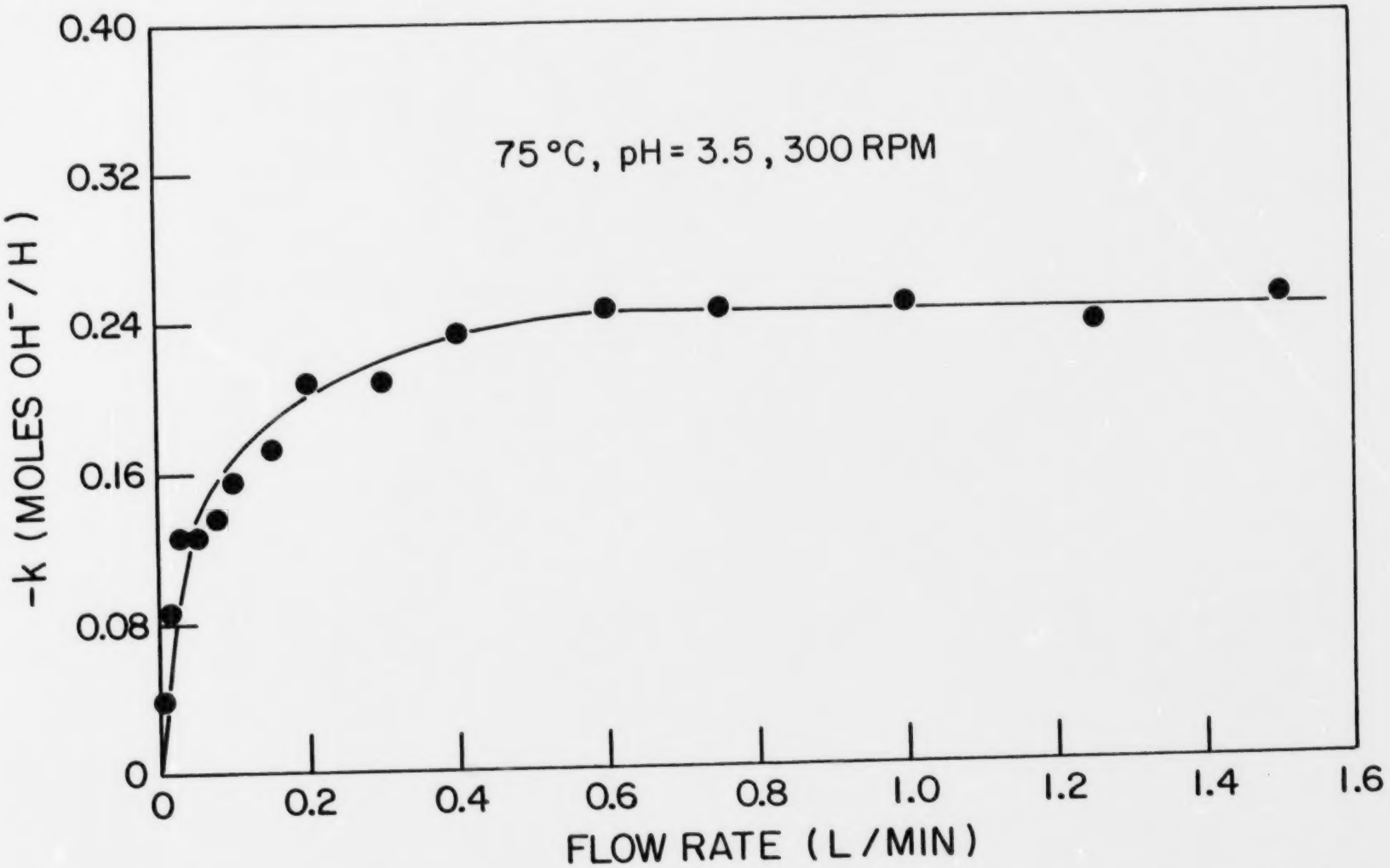


Fig. 2 - The effect of oxygen flow rate on the initial rate of goethite precipitation at 75°C, pH 3.5 and 300 rpm stirring speed.

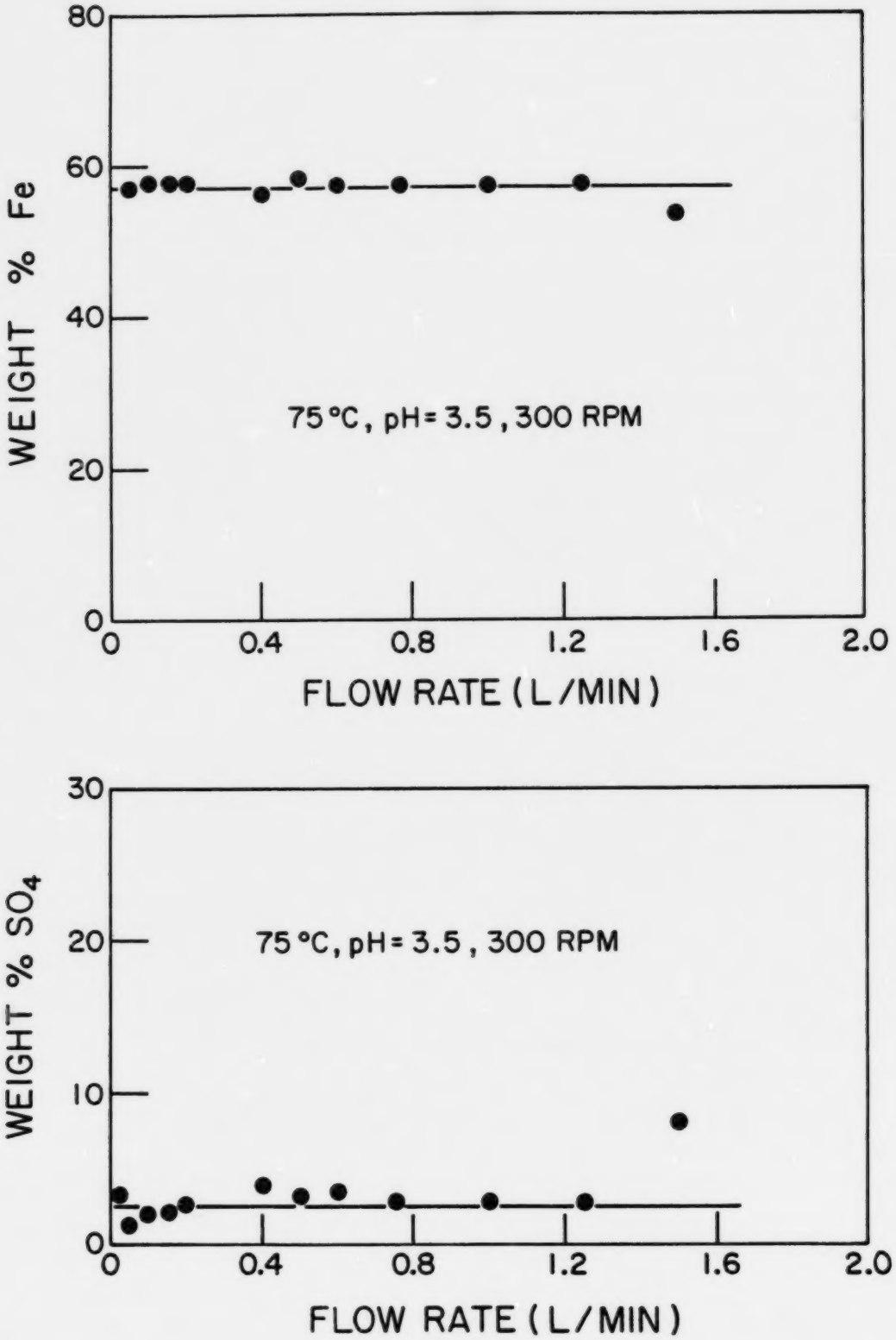


Fig. 3 - Effect of the oxygen flow rate on the iron (upper curve) and sulphate (lower curve) contents of the goethites formed at 75°C and pH 3.5.

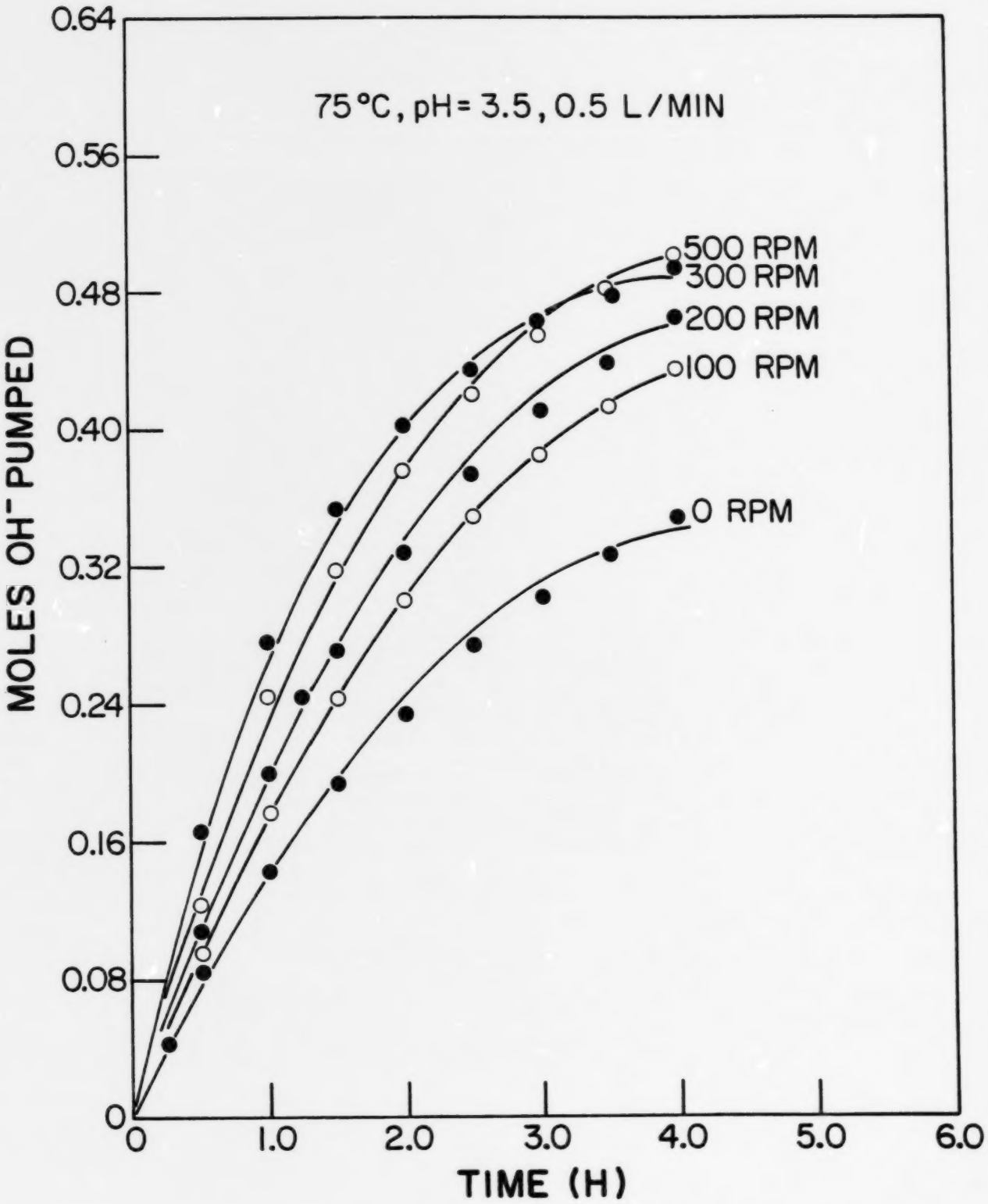


Fig. 4 - Typical reaction curves for goethite precipitation at 75°C, pH 3.5, 0.5 L/min $O_2$ flow rate and various solution stirring speeds.

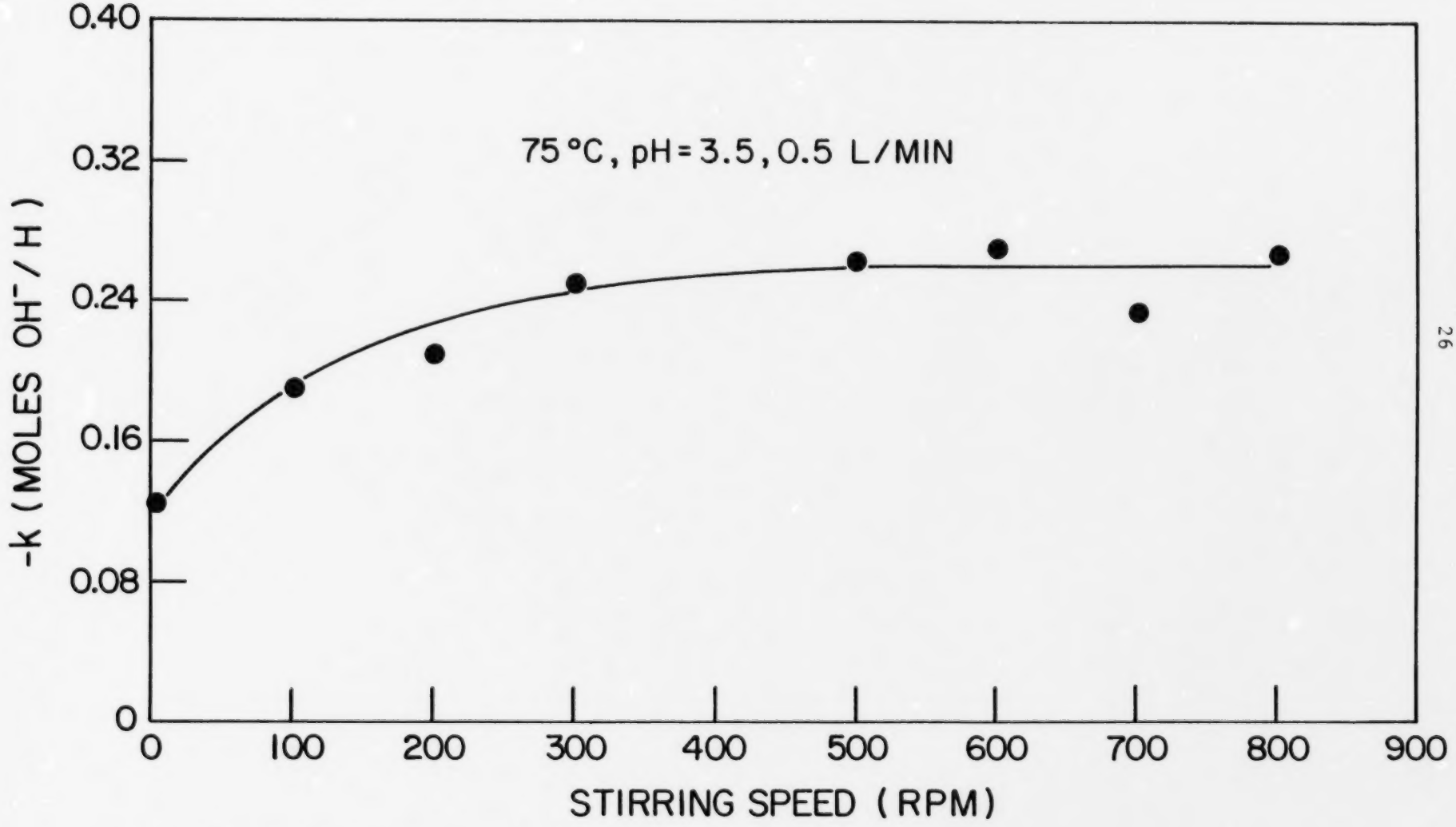


Fig. 5 - Effect of the solution stirring speed on the initial rate of goethite precipitation at 75°C, pH 3.5 and 0.5 L/min $O_2$ flow rate.

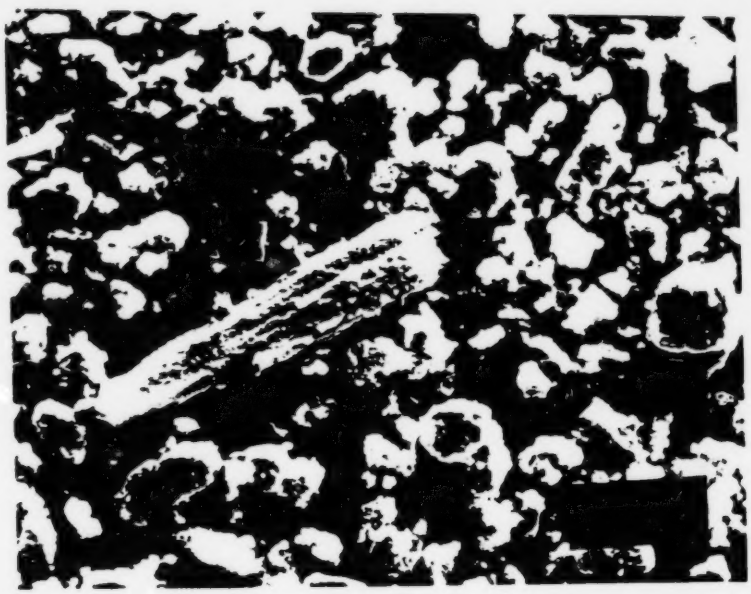

Fig. 6 - SEM micrograph of sample G-4 (dark) showing the two habits of FeO.OH, large platy aggregates and small globular masses.

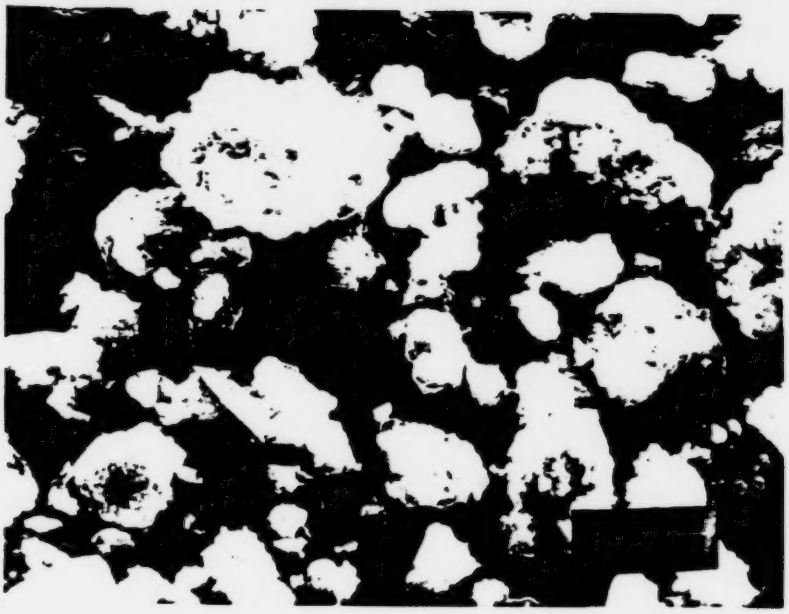

Fig. 7 - SEM micrograph of Sample G-4 (dark) showing the globular form of FeO.OH in more detail.

Fig. 8 - SEM micrograph of sample G-2 (light) showing the presence of numerous fine particles of FeO.OH.

Fig. 9 - SEM micrograph of a polished section of sample G-2 (light) showing several grains of FeO.OH.

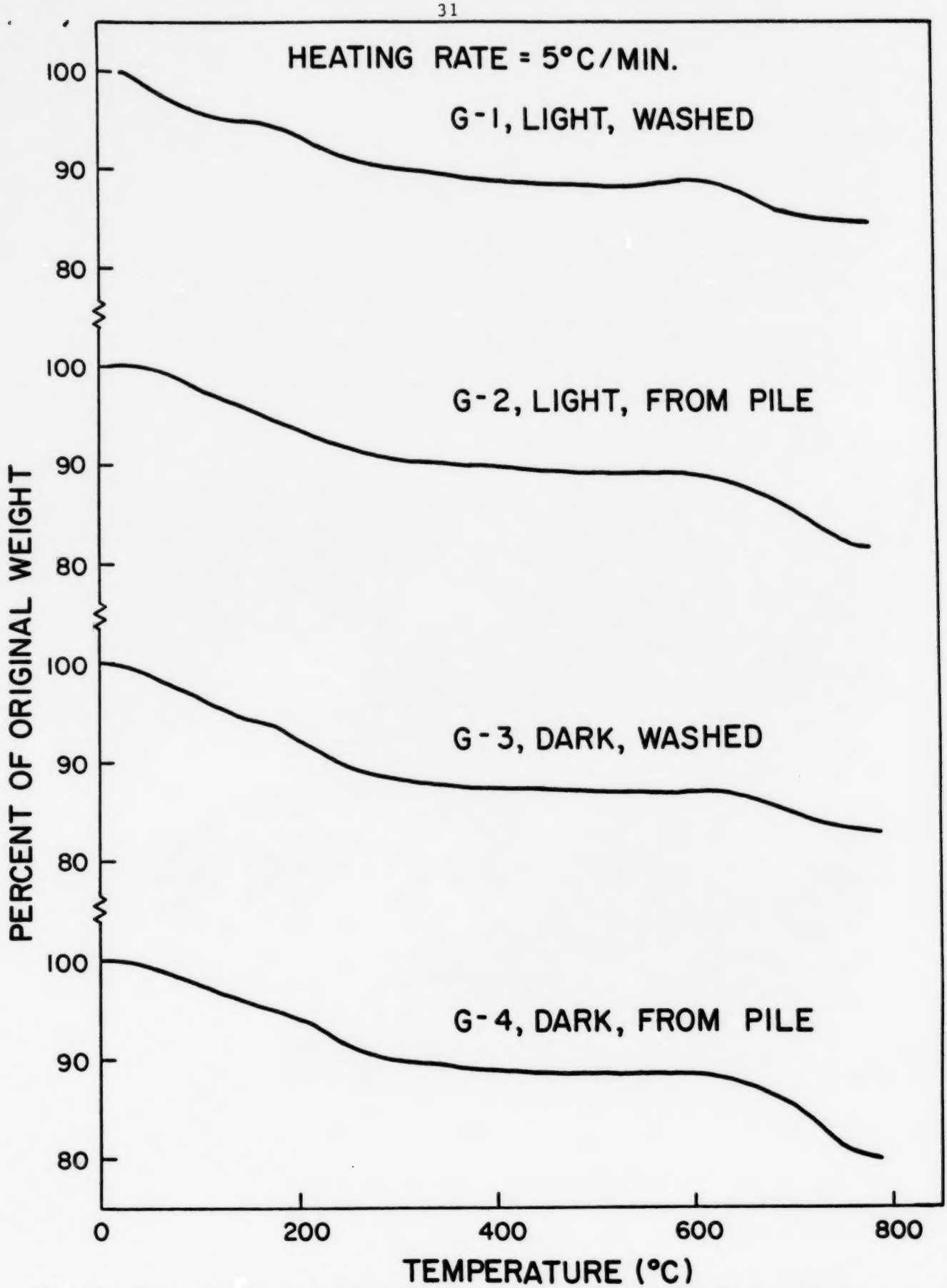


Fig. 10 - Thermogravimetric decomposition curves for the four goethite residues.

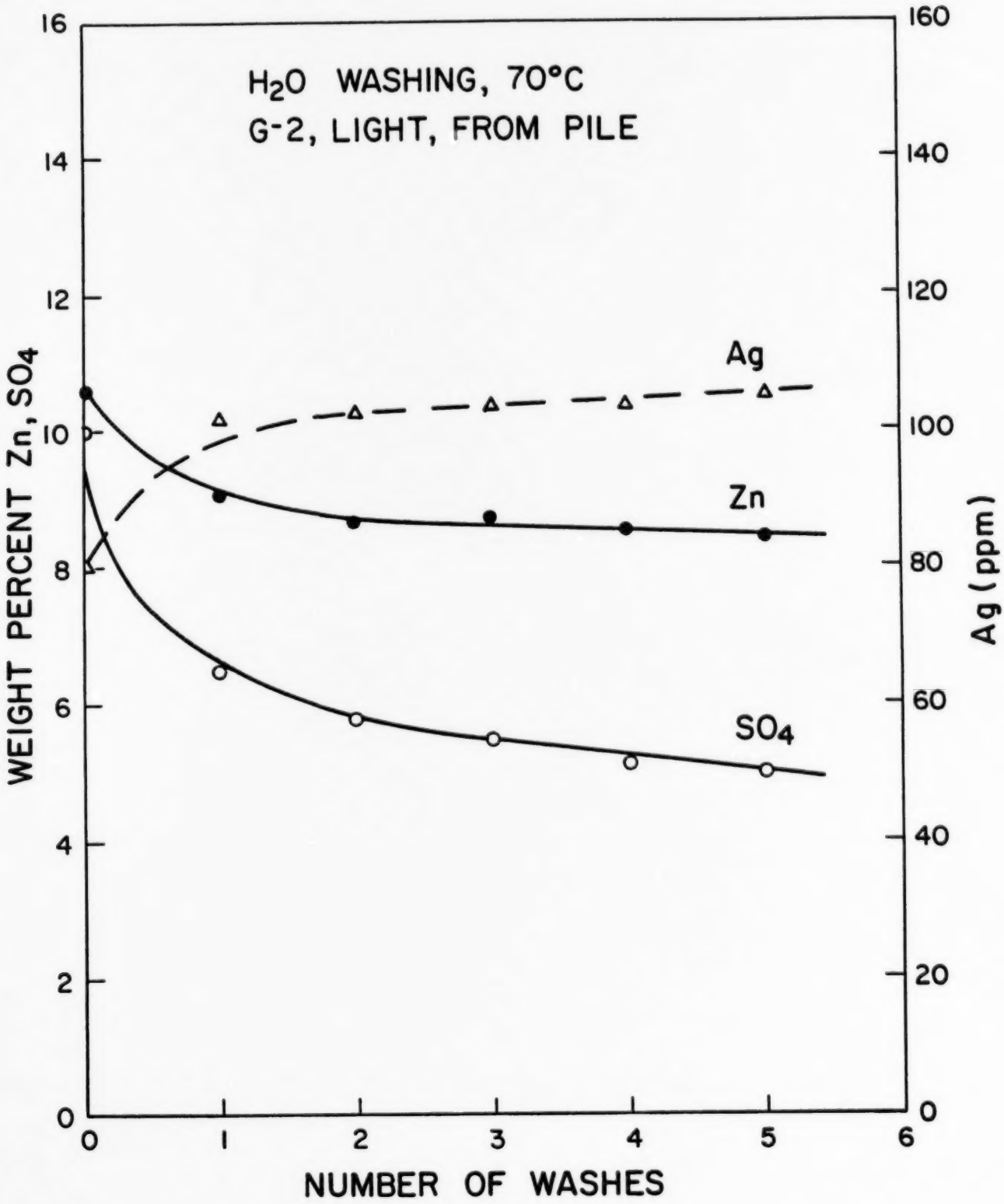


Fig. 11 - Effect of water washing on the composition of the goethite residues.

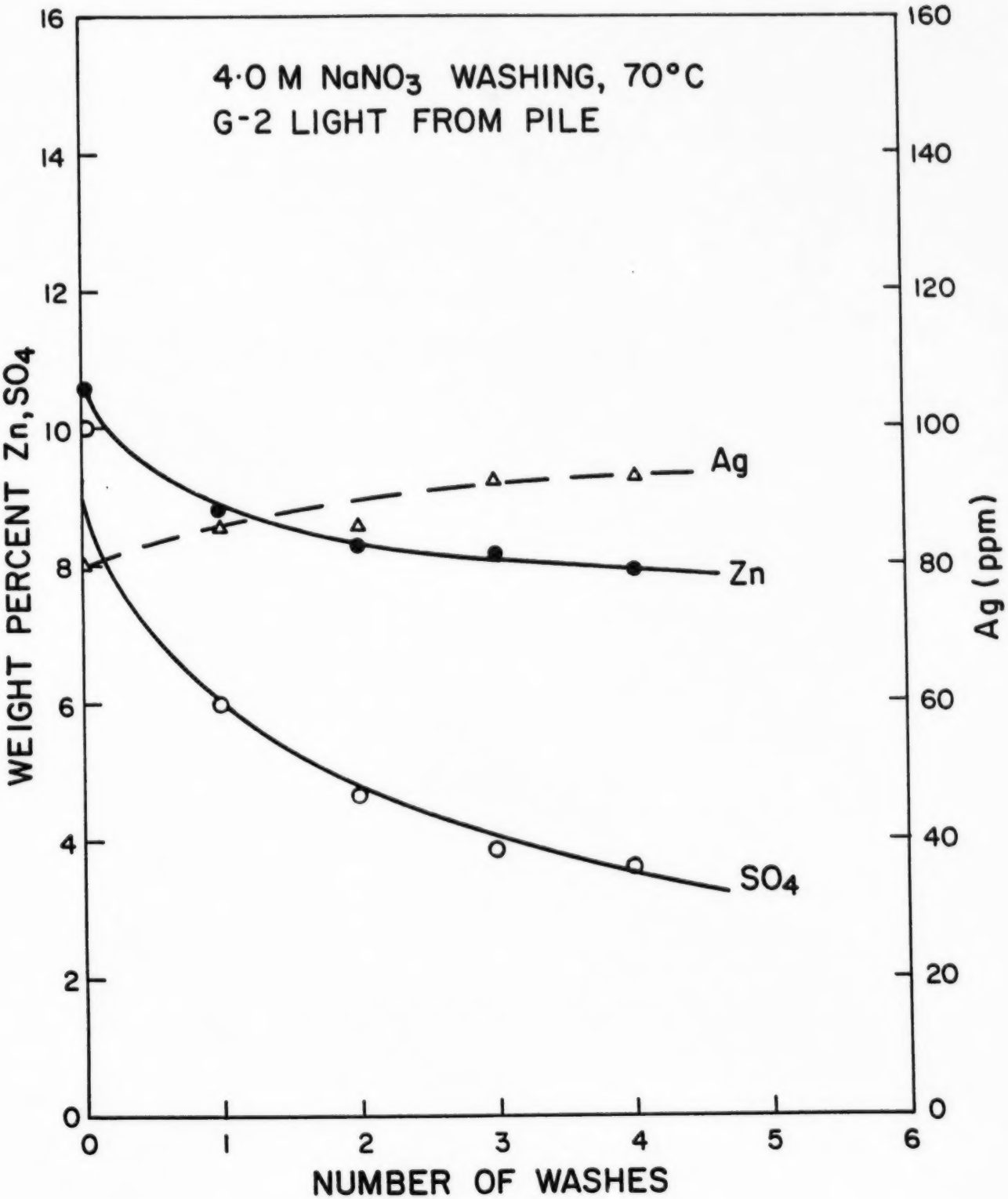


Fig. 12 - Effect of 4.0 M $NaNO_3$ washing on the composition of the goethite residues.

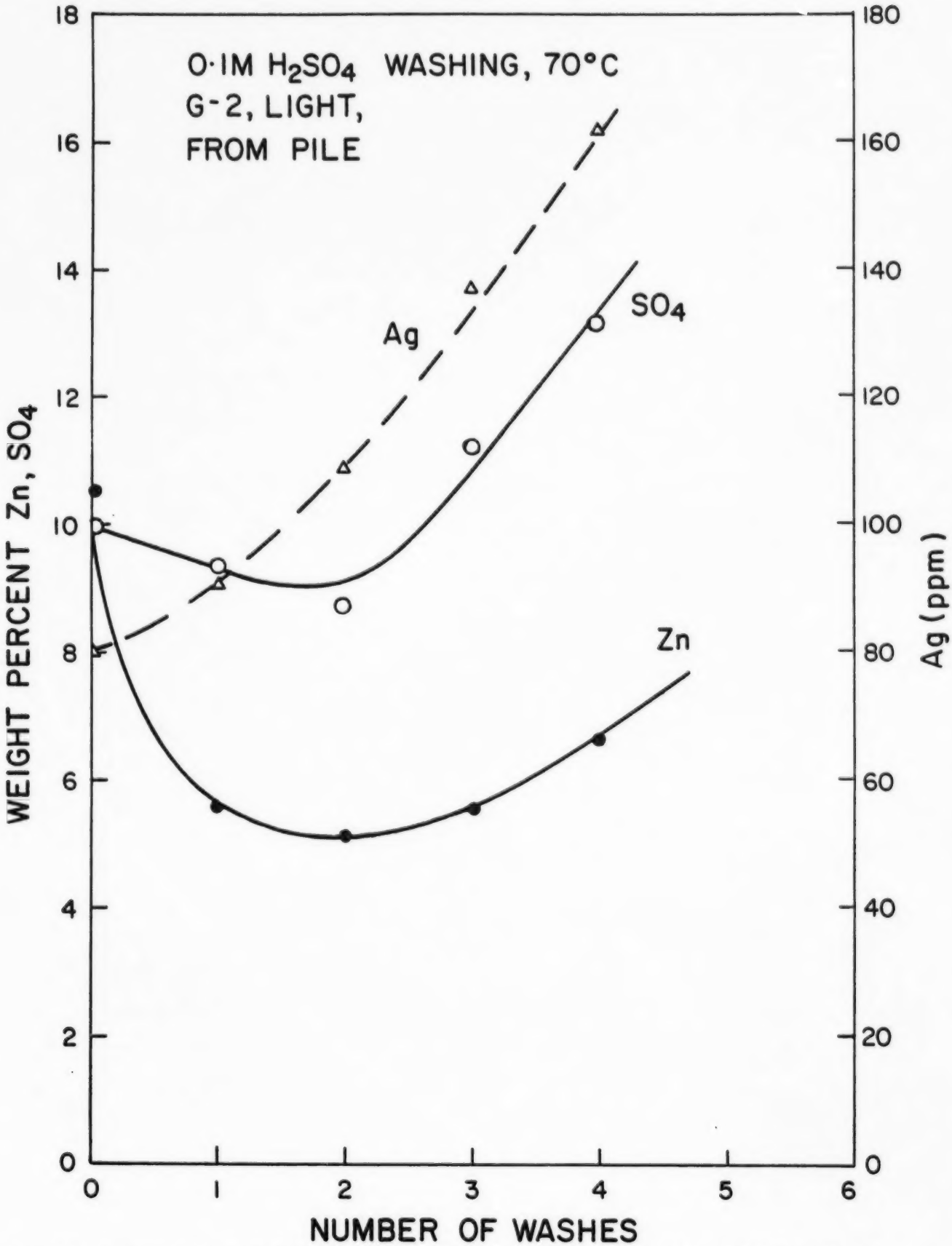


Fig. 13 - Effect of 0.1 M $H_2SO_4$ washing on the composition of the goethite residues.